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Disodium Tetracarbonylferrate

A Reagent for Acid Functionalization of Halogenated Polymers

Cezar Ungurenasu and Cornelia Cotzur

"P.Poni" Institute of Macromolecular Chemistry, Aleea Ghica Voda 41-A,
R-6600 Jassy, Romania

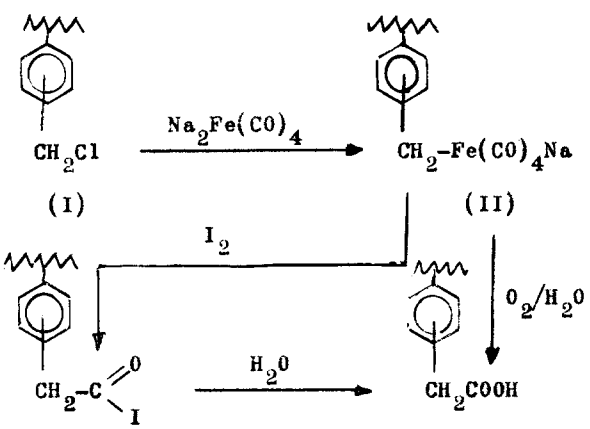
SUMMARY

The replacement of the chlorine atoms of chloromethylated polystyrenes by carboxyl groups via reaction with disodium tetracarbonylferrate and subsequent treatment with an oxidizing agent is described.

INTRODUCTION

Disodium tetracarbonylferrate, $Na_2Fe(CO)_4$, is a highly versatile and selective reagent, for converting alkyl halides to aldehydes (1), unsymmetrical ketones (2), or carboxylic acids, esters, and amides(3,4) in high yields and under mild conditions.

We now wish to report our preliminary results regarding the use of this reagent to the acid functionalization of chloromethylated polystyrenes as indicated in the following scheme :



Scheme 1

EXPERIMENTAL PART

The syntheses were carried out under argon, using carefully purified and dried reagents. Chloromethylated styrene-3%-divinylbenzene (SDVB-3), styrene-18%-divinylbenzene (SDVB-18), and styrene-27%-divinylbenzene (SDVB-27) copolymers were prepared according to published

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methods (5). Amounts of reactants are given in Table 1.

Table 1
Amounts of reactants used for preparation of tetracarbonylferrate functionalized polymers (II).

Sample	Chlorine content (%)	Amounts of reactants			
		Resin (g)	Hg (ml)	Na (g)	$Fe(CO)_5$ (g)
SDVB-3	18.25	2	6	0.63	2.5
SDVB-18	12.60	2	6	0.33	1.4
SDVB-27	15.00	2	6	0.40	1.7

1. Tetracarbonylferrate Functionalized Polymers (II)

Freshly prepared sodium amalgam and SDVB resin beads were suspended under stirring in 100 ml of THF; iron pentacarbonyl dissolved in 20 ml of THF was added dropwise under efficient stirring over 1.5 h period. The resulting mixture was stirred for an additional 36 h at room temperature. The resin beads were filtered, washed with THF-dioxane (1:1) and dried in vacuo at 70°C for 4 h to give the iron intermediate (II), whose structure was determined by IR spectroscopy (The presence of three ν_{CO} bands at 1986 (m), 1882 (s), and 1860 (s) cm^{-1} are consistent with the expected C_{3V} symmetry of CH_2-$Fe(CO)_4$ group).

2. Carboxylation of Iron Intermediate (II).

Method A : The suspension of intermediate (II) (2 g) in 50 ml of THF was cooled at -15°C and 10 ml of water were added followed by 2.5 g of I_2 dissolved in 25 ml of THF. After stirring 2 h at -15°C, the mixture was filtered, and the resin beads were sequentially washed with THF, ether, 1 N HCl, and water. The product was then dried in vacuo to constant weight and analysed.

Method B : The reaction was carried out in a pressure bomb containing a magnetic stirr bar. This apparatus was charged with 100 ml of THF, 2 g of intermediate (II) beads and 20 ml of water. After pressuring to 4 - 5 at(at room temperature) with O_2 the reaction mixture was stirred for 5 h at 25-30°C. The mixture was filtered, and the solid was sequentially washed with THF, 1 N HCl, water and ether. The product was then dried overnight at 60°C under vacuum.

RESULTS AND DISCUSSION

The reaction of $Na_2Fe(CO)_4$ with chloromethylated crosslinked polystyrene afforded the anionic iron complex (II) attached to resin. The

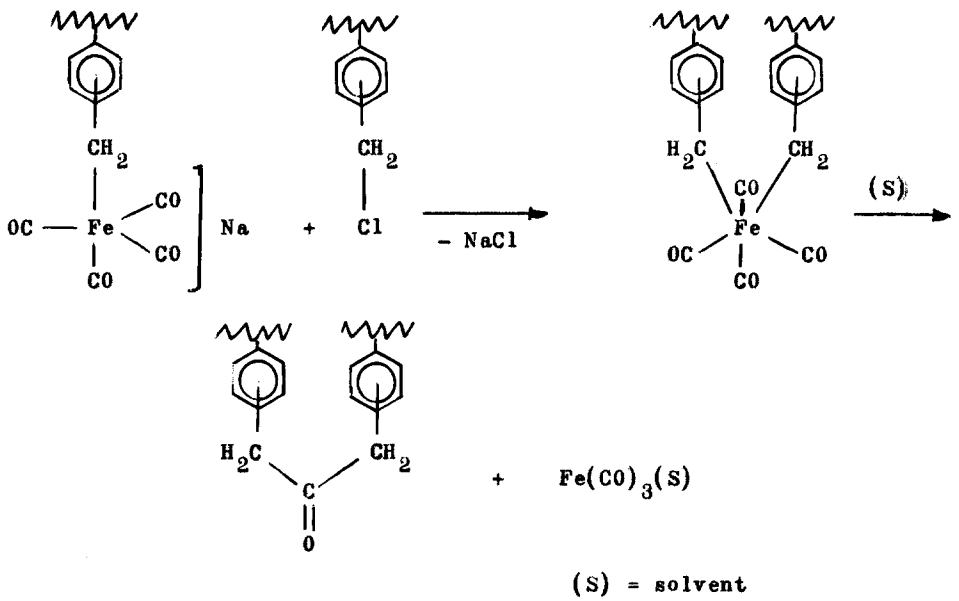
Table 2

Conditions and results of the acid functionalization of chloromethylated polystyrene.

Sample	Solvent	Residual Chlorine content %	Expected -COOH content %	Experimental -COOH content[a]	
				Method A %	Method B %
SDVB-3	THF	1.95	19.81	16.80	18.67
	Dioxane + THF	0.65	19.81	-	19.11
	Dioxane	3.43	18.08	14.92	16.20
SDVB-18	THF	6.57	7.52	6.22	6.83
SDVB-27	THF	9.00	7.48	5.40	6.11

(a) Calculated from ionic total exchange capacity data.

infrared spectrum of this intermediate shows three carbonyl stretching bands in the region 1860 - 1986 cm^{-1}, and a band for ketone carbonyl at 1712 cm^{-1}. It can be reasonably assumed that ketone linkages may be formed by side-side interaction as follows :



Scheme 2

As a probe for the formation of a crosslinkage , a soluble polystyrene was chloromethylated and then treated with $Na_2Fe(CO)_4$ to give a swellable polymer. The infrared spectrum of this polymer showed carbonyl stretching bands for both metal-bound and ketone CO-groups.

Polystyrene-bound carboxylic group was produced by treating the alkyl iron intermediate (II) with an oxidizing agent. The final product yields are limited mainly by the yields of anionic intermediate (II). Infrared spectra taken before and after functionalization shows that, in all cases, the C-Cl band (670 cm^{-1}) disappears, and a new band for the carboxylic group (1700 cm^{-1}) appears. Cleavage with molecular oxygen is essentially quantitative, and iron by-products are easily separated. The data of Table 2 show that resins with low degree of cross-linking are more reactive that highly cross-linked polymers.

Further work on the application of $Na_2Fe(CO)_4$ to introduction of $-CH_2CO(SH)$ group into polystyrenes and carboxylation of other polymers is in progress.

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